

# FIELD IONIZATION MASS SPECTROMETRIC ANALYSIS OF THE PHENALENONE-INDOLE COUPLING PRODUCT: THE NATURE OF INSOLUBLES FORMED IN DIESEL OILS

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## ABSTRACT

There is a growing acceptance of the theory that insolubles formed during storage of diesel oils result from the acid-catalyzed coupling of phenalenone and alkyl indoles. Field ionization mass spectrometric analysis of the sediments show prominent peaks due to alkyl indoles as well as those due to coupling products of phenalenone with one, two, three or four alkylindole moieties. However, conspicuous by their absence are peaks due to alkylphenalenones and phenalenones. FIMS analysis of a coupling product of phenalenone with indole, shows a prominent peak at 182 Da, that can be assigned to dihydrophenalenone. Most peaks in the spectrum, including minor ones, lend themselves to straightforward interpretation in terms of the known chemistry of coupling. Peaks corresponding to phenalene with one and two indole units were also prominent in the spectrum. Satellite peaks corresponding to hydrogenation and oxidation products are also present. Their presence indicates a multitude of redox reactions that accompany the coupling.

## INTRODUCTION

Storage of diesel fuels often results in the formation of deposits that cause problems with filtration and pumping of the fuels. Furthermore, some soluble gum is also formed that subsequently forms deposits on the hot engine parts causing additional problems. Numerous tests have been developed to predict the tendency of a fuel to form deposits.(1) Often, these tests require stressing the fuel at elevated temperatures, and the relevancy of such tests to storage conditions is not clear. Studies have also been conducted with dopants (2, 3), but again it is unclear whether the deposits formed in the presence of the dopant are the same as those formed under storage. An improved chemical understanding of the nature and causes of deposit formation is clearly needed. Chemical characterization of the sediments is valuable, because the agents responsible for their formation may be present at extremely low concentration in the fuel, but will necessarily be concentrated in the sediments.

We have previously shown that pyrolysis-field ionization mass spectrometry (Py-FIMS) is very useful in characterizing the deposits formed during storage of fuels.(4,5) We have found that there are a few patterns that repeat in the spectra for sediments from a variety of sources and that the filtered sediments and adherent insoluble gums are very similar in chemical nature with the sediments being enriched in the benzologs of the components in the gum. Peaks due to alkyl indoles are prominent in these spectra, and clusters of peaks corresponding to dimers and higher oligomers are also evident. In accord with the mechanism proposed by Hiley and Pedley (6), most of the prominent peaks in these spectra can be ascribed to the coupling products of phenalenone with one, two, three, or four alkylindole moieties. However, the peaks due to alkylphenalenones and phenalenones themselves are not very intense. In order to better understand the coupling mechanisms, we have prepared acid-catalyzed coupling products of indole and phenalenone, and examined it by field ionization mass spectrometry. Our objective was to determine if indeed the coupling product of phenalenone and indole does not give a strong peak signal corresponding to phenalene or phenalenone.

## EXPERIMENTAL

**Coupling Reaction.** Coupling product of indole and phenalenone (perinaphthenone) was prepared by adapting the procedure of Pedley and Hiley (6) for the synthesis of 2-methylindolylphenalene. Approximately 0.66 mmol indole was stirred overnight with an equivalent amount of phenalenone in the presence of *p*-toluenesulfonic acid (also 0.66 mmol) in methanol. The product was treated with excess potassium bicarbonate and extracted with ether. The mixture of coupling products was recovered by evaporating the ether.

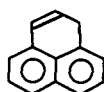
**Pyrolysis/Field Ionization Mass Spectrometry (Py/FIMS).** The technique of field ionization (FI) consists of passing vapors of the material to be analyzed through a region of intense electric field.(7) This mild technique for ionization results in the formation of only the molecular ions for most compounds, and because the ionization is generally not accompanied with any fragmentation it is particularly useful for analyzing complex mixtures. The FIMS system used in this study has been described elsewhere.(8) It consists of an activated tantalum foil field-ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. Approximately 50 µg of the sample is introduced via a heatable direct insertion probe. Mass spectral data of the evolving volatiles are collected by repeatedly scanning the magnet over a preset range while the sample is gradually heated from the initial temperature (sometimes as low as -78°C) to approximately 500°C. At the end of the run, the sample holder is retrieved and

weighed to determine the fraction that was devolatilized during the analysis. All the samples examined in this study were essentially 100% devolatilized during analysis. For a given sample, many spectra are collected, each representing a certain range of temperature. The individual spectra are added to obtain a spectrum of the total volatiles and produce a thermal evolution profile of total volatiles as well as of any given mass peak.

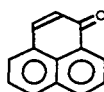
## RESULTS AND DISCUSSION

The FI-mass spectrum of the coupling product of indole (117 Da) and phenalenone (180 Da) is shown in Figure 1. This spectrum represents the sum of sixteen spectra (each comprising eight scans) collected during the heat up from ambient to 500°C. Because field ionization is generally not accompanied by fragmentation, the multitude of peaks in this spectrum corresponds to either multitude of compounds in the product, or extensive fragmentation due to pyrolysis in the FIMS probe. It is therefore instructive to examine the mass spectral data as a function of the probe temperature.

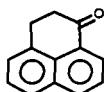
The spectrum of species that evolved almost immediately upon introduction of the probe into the inlet is shown in Figure 2a. This first set of peaks are at 117 Da (indole) and at 165, 166 (phenalenyl radical, and phenalene), and at 180 and 182 (phenalenone and dihydrophenalenone). The dihydrophenalenone peak is substantially more intense than that due to the parent phenalenone. A possible explanation is that the phenalenone underwent coupling, but the dihydro analog, which cannot undergo Michael addition, survived. Surprisingly, there were also peaks at 195 and 196 Da. The peak at 196 is most likely the methyl enol ether of the dihydrophenalenone, which was probably formed because the coupling was conducted in methanol as solvent. The peak at 195 Da is corresponding stable radical. The stability of the phenalenyl system is well recognized, and it is noteworthy that the radical species were seen with both phenalene and the enol ether; the latter being also capable of forming a phenalenyl radical with the loss of a hydrogen.



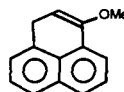
Phenalene (166)



Phenalenone (180)



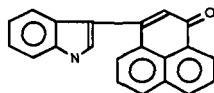
Dihydrophenalenone (182)



Dihydrophenalenone-enol methyl ether (196)

The fact that phenalene and dihydrophenalenone evolved at almost ambient temperatures suggests that they were present in the product mixture and were not a result of some thermal cracking of coupling products. This result further reinforces the facility with which phenalenone systems can undergo redox reactions (disproportionations), and lead to a multitude of products.

Upon warming the sample, the intensity of the peaks due to indole and phenalene and its analogs decreases, and a new set of peaks centered around 300 Da begins to evolve. They correspond to the coupling products of one phenalene and one indole residues. A representative spectrum is shown in Figure 2b. The simple coupling product of phenalenone and indole has a molecular weight of 295 ( $180 + 117 - 2 = 295$ ). Indeed, the peak at 295 is the most intense peak in the spectra acquired between 120 and 240°C, as well as in the sum spectrum (Figure 1). This peak is also accompanied by phenalene and the dihydrophenalenone analogs at 281 and 297 Da respectively. There is also a peak at 311, which is most likely due to the methyl ether of the corresponding enol. As before, strong peaks due to the phenalenyl radicals are present for the phenalene and the enol ether analogs of the coupling product. The coupling product is also accompanied by a dihydro derivative of the phenalene analog at 283 Da.



Indolenylphenalenone  
(295)

A similar pattern peaks around 410 Da for the bisindolenylphenalenones emerges as the sample is further heated to above 200°C (figure 2c). For the trisindolenylphenalenones, which also evolve in the 200 to 300°C range, however the expected peak at 325 Da ( $180 + 3 \times 117 - 6$ ) is not present to any significant extent. The peaks due to other analogs are present in reasonable intensity.

In the case of fuel sediments, similar peaks have been observed in their FI mass spectra.<sup>(5)</sup> However, we were not sure whether the products were present as simple oligomers or whether the oligomers were a result of thermal fragmentation of a polymer. Results obtained here show that the vaporization of the dimers and trimers in the FIMS probe occurs around 200 to 250°C. This temperature range corresponds well with the temperature at which these species evolved from the fuel sediments. Hence, we believe that, in the fuel sediments too, the dimers and trimers are present as such.

As mentioned above, the peak due to indole evolved at almost ambient temperatures. This peak was present in the spectra collected up to about 80°C, and was due to indole trapped in the product. The indole peak again appeared above about 180°C along with the evolution of coupling products.

This result suggests that at these temperatures, some of the coupling products do fragment to liberate indole fragments.

## CONCLUSION

We have prepared an acid-catalyzed coupling product from the reaction of indole with phenalenone and analyzed it by FIMS. The mass spectrum shows the presence of the expected indolenylphenalenone, bisindolenylphenalenone, trisindolenylphenalenone, and so on. It also shows peak corresponding to redox derivatives and methyl ethers. The temperature resolved mass spectral data are consistent with simple evaporation of the oligomers and not due to thermal fragmentation.

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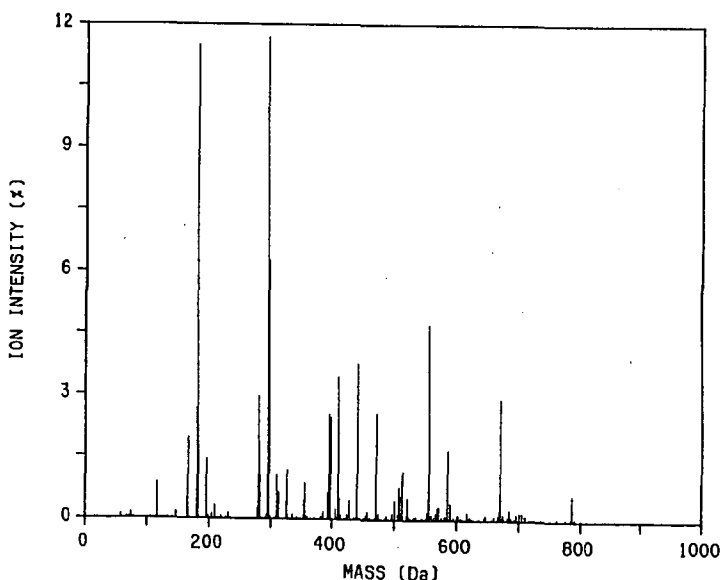


Figure 1. FI mass spectrum of the total volatiles from phenalenone-indole coupling product collected from 30 to 500°C.

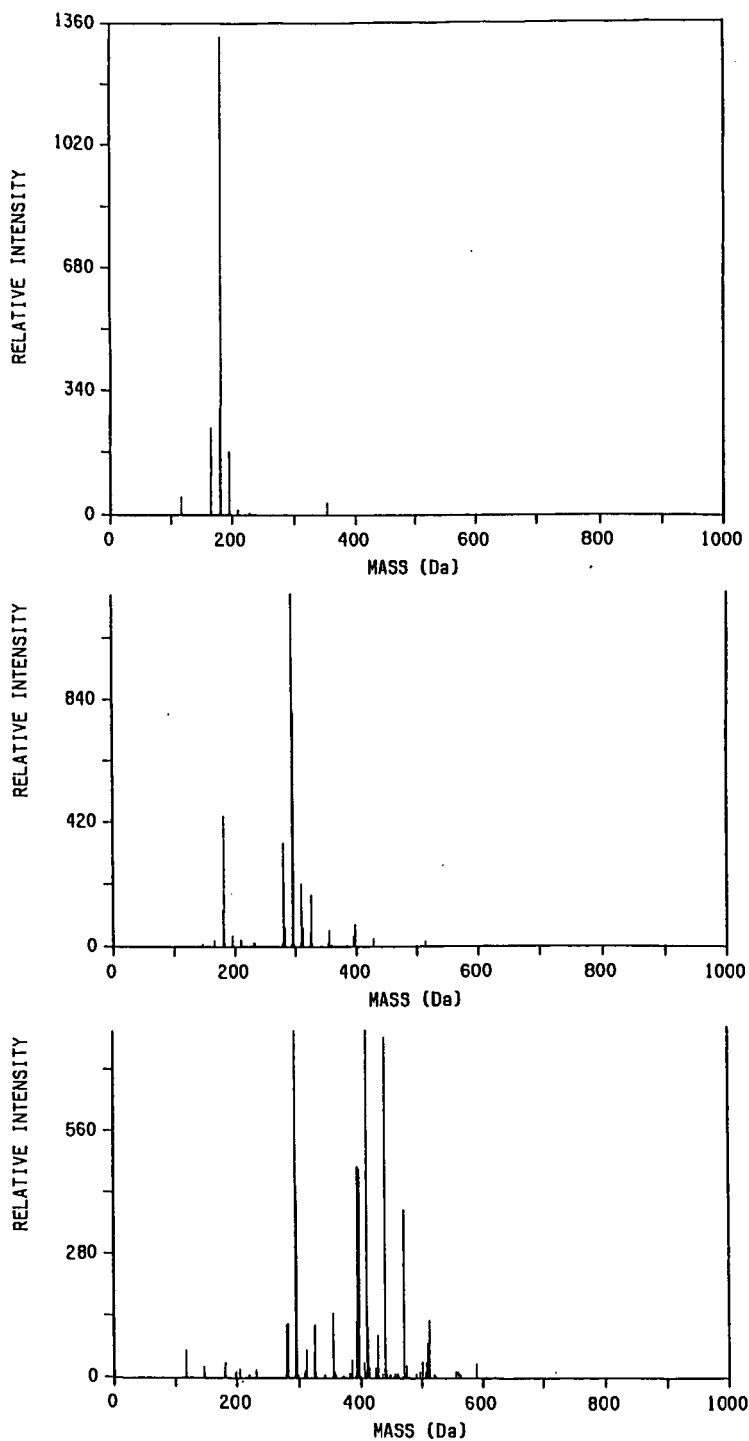


Figure 2. FI mass spectrum of the volatiles from the phenalene-indole coupling evolving in the temperatures ranges (a) 46651°C (b) 148 to 165°C, and (c) 211 to 238°C.